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SHORT COMMUNICATION

Acetylation of Chinese bamboo flour and thermoplasticity

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Abstract: Chinese bamboo flour was chemically modified by acetylation with acetic anhydride by using trichloroacetic acid as an activation agent and the optimized condition for acetylation of bamboo flour was determined as the trichloroacetic acid amount 6.0 g per 1.5-g bamboo flour, ultrasosonication duration 40 min and the reaction time 1 h at 65°C. The composition, microstructure and thermal behavior of acetylated bamboo flour were preliminarily characterized by FT-IR, DSC and SEM etc. The acetylated bamboo flour can be molded into sheets at 130°C and 10 MPa, indicating the modified bamboo flour possesses thermalplastic performance.

Keywords: acetylation; thermoplasticity; bamboo flour; modification; trichloroacetic acid

Introduction

Greenhouse effect has been becoming one of the most serious environmental concerns (Tung and Yamamoto 2004). Polymer composites based on fossil oil cause a heavy burden from the viewpoint of sustained development. A large amount of carbon dioxide is released when they are further treated for example by burning. Alternatively, bioplastics and natural plant fibers have recently attracted considerable attention as ecological and green materials.

Bamboo is a natural lignocellulosic based composite material, which is abundant in Asia and South America. It grows faster than any other kind of wood species and can mature within three to eight years. Bamboo has been traditionally used to construct village houses as a structural material for its light weight and high mechanical strength, and industrial development of bamboo has broadened its application areas. Modified bamboo can be used as reinforcement filler for plastics (Okubo et al. 2004) in which thin fibers are extracted from raw bamboo using a steam explosion method (Okubo et al. 2004; Takatani et al. 1998). In order to improve dispersibility of bamboo fibers within plastic matrix and interfacial strength, it is urgent to modify the bamboo fibers. In this paper, we report a modification by acetylation to bamboo flour and preliminary results of glass transition and microstructure of the modified bamboo flour as well.

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Materials and methods

The bamboo material was collected in Fujian Province, China, and crushed into bamboo flour. Bamboo flour was separated through a mesh 80#. After bamboo flour was treated by trichloroacetic acid (TCA) under ultrasonication, it was further reacted with acetic anhydride catalyzed using perchloric acid at 65°C for a desired duration. The system was poured into distilled water under stirring for two hours. After being filtered and washed until to be neutral, the modified bamboo flour was dried at 105°C for 12 h. The weight percent gain (WPG) after acetylation was calculated on the basis of the original weight of untreated bamboo flour. Acetylated or original bamboo flour was pressed into thin sheets about 10×5×0.5 cm under a pressure of 10 MPa at 130°C for 10 min.

All samples were thoroughly washed with distilled water to remove residual anhydride and acetic acid. The dried samples were pressed into pellets together with potassium bromide (KBr) for characterization with Nicolet 5700 FT-IR spectrophotometer. After dried at about 105°C until the weight unchanged, glass transition of the samples was carried out using METTLER 822e differential scanning calorimeter at a scanning rate of 10°C /min. Scanning electron microscopy (SEM) measurements were performed with a JSM-6380LV apparatus. The samples were vacuum sputtered with Au. The morphology of bamboo flour was observed with a polarization microscope (Leica DM LP).

Results and discussion

Powell (1986）reported a simple procedure for acetylation of hardwood and softwood flakes without cosolvents or catalysts, however, modification degree is rather limited. Yu and Li (1994) used trifluoroacetic acid (TFA) to activate the acetylation for

Chinese pine and fir, in order to enhance the modification degree, but the procedure is expensive. Bamboo flour is mainly composed of cellulose, hemicellulose and lignin. It is required to find an effective and economic approach to chemically modify bamboo flour. Due to the complex constituents of bamboo flour, the acetylation extent is described by WPG before and after bamboo flour is modified. TCA was employed as activating agent. The effect of TCA amount on the acetylation extent is shown in Fig. 1. With the increase of TCA amount, WPG was increased almost in a linear style. When TCA amount was further increased to a higher level, WPG began to decrease. The maximum WPG about 45% was achieved when the weight ratio of TCA/ bamboo flour reached 6/1.5. The modification kinetics is diffusion controlled (Powell et al. 1994). It is noticed that TCA can facilitate acetic anhydride to diffuse easier into the fiber by breakage the crystalline structure of bamboo fiber, thus accelerating the acetylation reaction between acetic anhydride and the bamboo flour fiber.

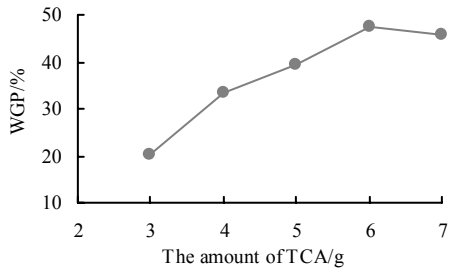

Fig. 1 Acetylation degree of bamboo flour as a function of TCA amount

Fig. 2 Polarizing optical microscope images of bamboo flour before (a) and after (b) being activated under sonication (magnification: 100)

The morphology change of bamboo-flour fiber before and after being treated with TCA under sonication was compared as shown in Fig. 2. The whole fibers after being treated can be distinguished under microscope, meaning that TCA has diffused into the fibers. A maximum WPG is achieved when activation time reached 40 min. As shown in Fig. 3, the maximum WPG was achieved after a reaction for one hour. With further prolongation in reaction time, WPG was slightly decreased. Another key factor to influence the acetylation degree is activation time under sonication. As shown in Fig. 4, WPG increased with activation time to a plateau after 40 min. Therefore, activation time is fixed 60 min for all modification batches. The optimized condition for acetylation of bamboo flour is thus finally determined as the TCA amount 6.0 g per 1.5-g bamboo flour, ultrasosonication duration 40 min and the reaction time 1 h at 65°C

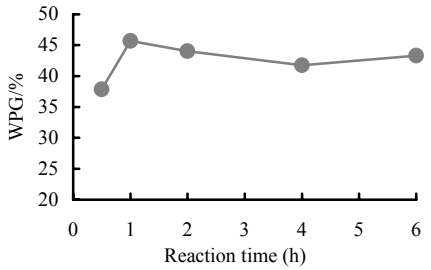

Fig. 3 Acetylation degree of bamboo flour as a function of reaction time

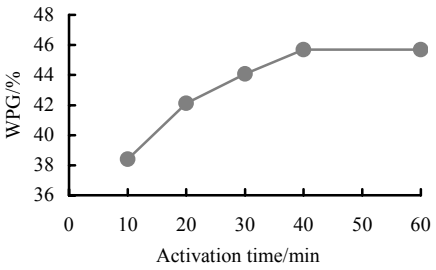

Fig. 4 Acetylation degree of bamboo flour as a function of activation time

The acetylation is further confirmed by FT-IR spectra as shown in Fig. 5. By comparison of the original and acetylated bamboo flour samples, three major differences were found: 1) a reduction in the hydroxyl (O-H) stretching band (3200–3500·cm^{-1}), 2) an increase in the carbonyl (C=O) stretching region (1735–l765·cm^{-1}), and 3) an increase in the carbon-oxygen (C-O) stretching region (1000–1245·cm^{-1}). Because of the high crystallinity degree of the cellulose (almost 70%), to break the crystalline structure of bamboo fiber completely is impossible in fact. Meanwhile, the full reaction between hydroxyl and acetic anhydride is impractical either. The reduction rather than disappearance in the hydroxyl (O-H) stretching band appropriately accord with this.

Because there are still a certain amount of hydroxyls not reacting with acetic anhydride, the material will absorb water in the air. The samples were dried at about 105°C until the weight unchanged to avoid the water impaction on their DSC behavior.

Thermal behavior of bamboo flour is complex as shown in Fig. 6. From DSC curve of the original bamboo flour, there exists a single broad exothermic region around 300°C, corresponding to a cracking of cellulose and hemicellulose accompanied with the elimination of water. Meanwhile, monosaccharide, oligosaccharide and ramification of furan are derived (Nguyen et al. 1981). The small endothermic peak at about 365°C may be related with the cracking of glycogen. For the acetylated bamboo flour, there exists a remarkable glass transition around 265°C, which is not found in the original bamboo flour. The preliminary results indicate that the acetylated bamboo flour has possessed thermoplasticity, which will be important for further processing. As shown in Fig. 7, the original bamboo flour can not be molded into sheets. After being acetylated, bamboo flour can be molded into a sheet with the bamboo fibrils disappeared. The further investigation on molding process and properties of the sheets from acetylated bamboo flour with varied modification degrees is in progress.

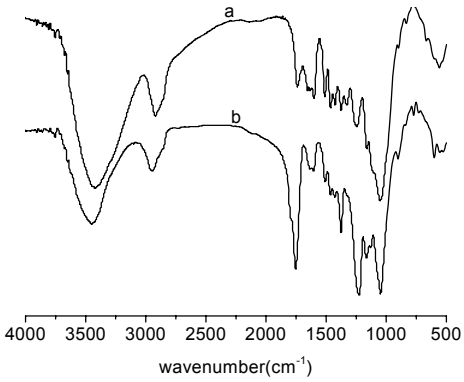

Fig. 5 FT-IR spectra of bamboo flour before (a) and after (b) being acetylated

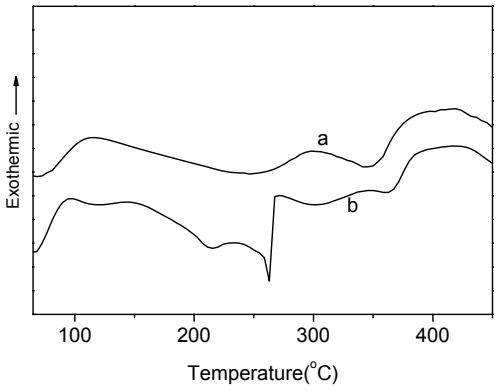

Fig. 6 DSC results of bamboo flour before (a) and after (b) being acetylated

Conclusion

Natural bamboo fibers are chemically modified by acetylation to bring new properties. The modification condition has been optimized. The composition, microstructure and thermal behavior have been preliminarily characterized. Especially, the acetylated bamboo flour can be molded into sheets. It is promising to prepare such natural mold samples, which can be self-reinforced with the fibers. However, there are still more efforts needed to be done for the application of the product in the industry market.

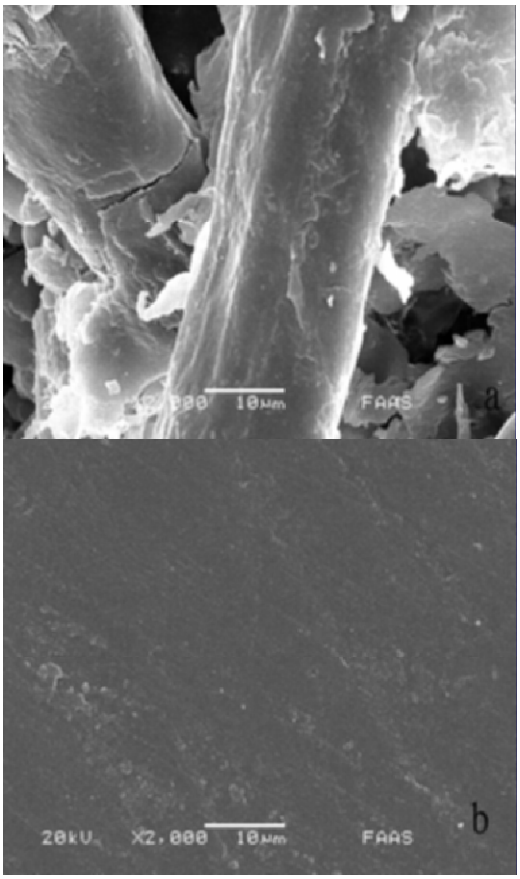

Fig. 7 SEM images of bamboo flour before (a) and after (b) being acetylated

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